5). The role of a solvent molecule may be understood by considering its interaction with the coordinated oxygen atom in $V(acac)_3$. The V–O bond is weakened, and the effective charge of the V^{III} ion increases through such an interaction to facilitate the formation of II* or IV* by the nucleophilic attack of Hacac or H_2O.[27]

The increase in k_0 in the presence of trichloroacetic acid in Hacac (Table IV) is also regarded as the acid catalysis, the proton interacting with the coordinated oxygen.[23]

Comparison with Related Reactions. Second-order rate constants and activation parameters of substitution reactions of $V^{III}O_6$-type complexes including ligand exchange (k_{ex}), anation (k_f), and solvolysis (k_s) are collected in Table V. The present k_{ex} (k_a) value is smaller by an order of 10^3–10^7 than the k_{ex}, k_f, and k_s values for the reactions of $[V(H_2O)_6]^{3+}$ and $[V(Me_2SO)_6]^{3+}$ with unidentate nucleophiles.[2-6] Such an inertness is in line with that in the exchange of malonato ligand in aqueous solution (cf. **2** in Table V).[29] The reaction product between $[V(Me_2SO)_6]^{3+}$ and 2,2′-bipyridine or sulfosalicylic acid in Me_2SO (**8** and **9** in Table V)[5] can contain the bidentate ligand as either unidentate or chelate. The small rate constants of the backward reactions suggest the presence of chelated species.

Most of the activation entropies in Table V are similar to one another. All these reactions seem to proceed via an associative rate-determining step, regardless of the dentate number of the ligands. (The anation of NCS^-,[2] N_3^-,[4] and $HC_2O_4^-$[7] for $[V(H_2O)_6]^{3+}$ was suggested to proceed via an associative mechanism). On the other hand, the ΔH^* values scatter and seem to be responsible for determining the mechanism.) The inertness of the present reaction is attributed to the large ΔH^* value.

The sequence of the exchange rates of $M^{III}(acac)_3$ in Hacac is obtained as follows:[9,10] $Fe^{III} > V^{III} \gg Co^{III} > Cr^{III} > Ru^{III} > Rh^{III}$. The first-order rate constant k_a value for V^{III} is 25 times smaller than for Fe^{III} and is larger than that for Co^{III} by a factor of 10^6, at 25 °C.

Registry No. $V(acac)_3$, 13476-99-8; Hacac, 123-54-6.

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Synthesis and Spectroscopic Study of η^5-$C_5H_5(CO)_2Fe[C(XR)YR]^+$ Carbene Complexes, Where X and Y Are O, S, Se, and/or NR

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A variety of $Cp(CO)_2Fe[C(XR)YR]^+$ (X = S; Y = O, S, Se) carbene complexes are readily available from $Cp(CO)_2Fe(CS)^+$ by reaction with RY^- to form $Cp(CO)_2FeC({=}S)YR$, followed by alkylation with CH_3SO_3F or $CH_3SO_3CF_3$. Similar treatment of $CpFe(CO)_3^+$ leads to $Cp(CO)_2Fe[Y(CH_3)Ph]^+$ compounds rather than carbene complexes. The reactions of $Cp(CO)_2Fe[C(SCH_3)OCH_3]^+$ with alcohols and $Cp(CO)_2Fe[C(SCH_3)_2]^+$ with dithiols yield $Cp(CO)_2Fe[C(OR)OCH_3]^+$ and $Cp(CO)_2Fe[\overline{CS(CH_2)_nS}]^+$ (n = 2, 3) carbene complexes, respectively. The thiooxocarbene complex $Cp(CO)_2Fe[C(SCH_3)OCH_3]^+$ undergoes facile thermal rearrangement to a binuclear species, $[Cp(CO)_2Fe]_2SCH_3^+$. Reaction of $Cp(CO)_2Fe[C(SCH_3)_2]^+$ with $LiAlH_4$ yields $Cp(CO)_2Fe[C(SCH_3)_2H]$ which may be converted to an unstable secondary carbene complex, $Cp(CO)_2Fe[C(SCH_3)H]^+$, by reaction with CF_3SO_3H. These new carbene complexes, and other known carbene complexes, are studied by IR, ^1H NMR, and ^{13}C NMR spectroscopy to determine the electronic effects of the XR and YR groups; an order of relative π-stabilization ability is established ($N \gg Se \geq S > O$). Trends in the chemical shifts of the carbene carbons in the ^{13}C NMR spectra of the $Cp(CO)_2Fe[C(XR)YR]^+$ complexes are also observed.

Introduction

Transition-metal carbene complexes are of great interest as they are postulated as intermediates in catalytic processes, most notably in the Fischer–Tropsch reaction[2a] and in olefin metathesis.[2b] A better understanding of chemical, physical, and electronic factors which influence model carbene systems should lend insight into these catalytic processes. The interesting chemical behavior found for $Cp(CO)_2Fe$[dithiocarbene]$^+$ complexes[3] (Cp = η^5-C_5H_5) has prompted us to investigate the $Cp(CO)_2Fe$[carbene]$^+$ system further.

Carbon-13 NMR spectroscopy has proven to be a valuable tool in organometallic chemistry.[4-6] Analysis of carbene complexes by ^{13}C NMR spectroscopy is especially interesting because of the high sensitivity of the carbene carbon resonance to changes in the electronic environment.[7] In this report, we present the synthesis of a variety of iron carbene complexes incorporating O, S, and Se into the carbene ligands. These complexes, and other carbene complexes reported previously,[3,8] are analyzed by means of IR, ^1H NMR, and ^{13}C NMR spectroscopy with emphasis on the relative π-stabilization abilities of the heteroatoms in the carbene ligands.

Results and Discussion

Preparation of Carbene Complexes from $Cp(CO)_2Fe(CS)^+$. The bis(methylthio)carbene complex $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ (Ia) has been prepared in 69% yield from $Cp(CO)_2FeC({=}S)SCH_3$ (which may be obtained from the re-

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(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Energy Research, Office of Energy Research, Grant WPAS-KC-03-02-01.

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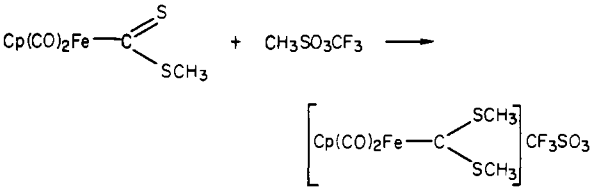
Table I. IR Spectra of the New Complexes and of Other Pertinent Carbene Complexes in CH_2Cl_2

complex	ν(CO), cm^{-1}	k(CO),[a] mdyn/A
$\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$[b] (Ia)	2058 (s), 2017 (s)	16.77
$\{Cp(CO)_2Fe[C(SCH_3)_2]\}CF_3SO_3$ (Ib)	2055 (s), 2014 (s)	16.72
$Cp(CO)_2FeC(=S)SePh$ (IId)	2032 (s), 1983 (s)	16.28
$\{Cp(CO)_2Fe[C(SCH_3)OCH_3]\}PF_6$ (IIIa)	2062 (s), 2019 (s)	16.82
$\{Cp(CO)_2Fe[C(SCH_3)OPh]\}PF_6$ (IIIb)	2060 (s), 2019 (s)	16.80
$\{Cp(CO)_2Fe[C(SCH_3)SPh]\}PF_6$ (IIIc)	2057 (s), 2016 (s)	16.75
$\{Cp(CO)_2Fe[C(SCH_3)SePh]\}PF_6$ (IIId)	2058 (s), 2019 (s)	16.78
$\{Cp(CO)_2Fe[C(SCH_3)OCH_3]\}CF_3SO_3$ (IV)	2060 (s), 2017 (s)	16.78
$\{[Cp(CO)_2Fe]_2SCH_3\}CF_3SO_3$ (V)	2056 (vs), 2039 (s), 2003 (vs, br)	
$\{Cp(CO)_2Fe[S(CH_3)Ph]\}PF_6$ (VIIa)	2064 (s), 2022 (s)	16.86
$\{Cp(CO)_2Fe[Se(CH_3)Ph]\}PF_6$ (VIIb)	2057 (s), 2017 (s)	16.76
$\{Cp(CO)_2Fe[\overline{CS(CH_2)_2S}]\}PF_6$ (VIIIa)	2065 (s), 2024 (s)	16.88
$\{Cp(CO)_2Fe[\overline{CS(CH_2)_3S}]\}PF_6$ (VIIIb)	2057 (s), 2015 (s)	16.74
$\{Cp(CO)_2Fe[C(OCH_3)_2]\}PF_6$[c] (IX)	2068 (s), 2020 (s)	16.87
$\{Cp(CO)_2Fe[C(OCH_3)_2]\}CF_3SO_3$ (Xa)	2063 (s), 2016 (s)	16.80
$\{Cp(CO)_2Fe[C(OCH_3)OCH_2CH_3]\}CF_3SO_3$ (Xb)	2064 (s), 2017 (s)	16.82
$Cp(CO)_2Fe[C(SCH_3)_2H]$[d] (XI)	2018 (s), 1968 (s)	16.04
$\{Cp(CO)_2Fe[C(SCH_3)H]\}CF_3SO_3$ (XII)	2067 (s), 2026 (s)	16.91
$\{Cp(CO)_2Fe[C(OCH_3)H]\}PF_6$[e] (XIII)	2085 (s), 2043 (s)	17.21
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_2NH}]\}PF_6$[b]	2053 (s), 2003 (s)	16.61
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_3NH}]\}PF_6$[b]	2051 (s), 2000 (s)	16.57
$\{Cp(CO)_2Fe[C(SCH_3)SCH_2CH_3]\}PF_6$[b]	2060 (s), 2017 (s)	16.78

[a] Reference 22. [b] Reference 3. [c] Reference 13. [d] In hexanes. [e] Reference 24, in CH_3NO_2.

action of $Cp(CO)_2Fe^-$ with CS_2 and CH_3I[9] or by reaction of $Cp(CO)_2Fe(CS)^+$ with CH_3S^- [10]) by alkylation with CH_3SO_3F followed by PF_6^- exchange.[3] Methyl trifluoromethanesulfonate, $CH_3SO_3CF_3$, has been shown to alkylate the thioformyl ligands of $X(CO)(L)_3OsC(=S)H$ (X = Cl, Br; L = CN(p-tolyl), PPh_3) to give secondary carbene complexes, $X(CO)(L)_3Os[C(SCH_3)H]^+$,[11] and it also reacts with $Cp(CO)_2FeC(=S)SCH_3$ to give the $CF_3SO_3^-$ (triflate) salt of Ia in excellent yield (eq 1).



(1)

Ib (87%)

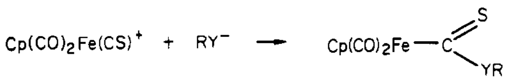
The significant improvement in yield over the previously reported route[3] may be largely due to the elimination of the anion-exchange step. Complex Ib crystallizes very readily and has stability and solubility characteristics similar to those of Ia.[3]

Table II. ^1H NMR Spectra of the New Complexes and Other Pertinent Carbene Complexes in Acetone-d_6 (τ)[a]

complex	C_6H_5	C_5H_5	OCH_3	SCH_3	other resonances
Ia[b]		4.43		6.73	
Ib		4.34		6.69	
IId[c]	2.73	5.09			
IIIa		4.34	5.09	7.33	
IIIb[d]	2.53 (m)	4.80		7.22	
IIIc[d]	2.33 (br)	4.74 (br)		6.88	
IIId[d]	2.31 (br)	4.69 (br)		6.84	
IV		4.33	5.09	7.33	
V		4.48		7.88	
VIIa	2.41 (m)	4.30		6.99	
VIIb	2.42 (m)	4.32		7.06	
VIIIa		4.36			5.87 (2 CH_2)
VIIIb		4.50			6.57 (t, 2 CH_2), 7.45 (m, CH_2)
IX[e]		4.35	5.58		
Xa		4.34	5.59		
Xb		4.36	5.63		5.18 (q, OCH_2), 8.50 (t, CH_3)
XI[f]		5.07		7.80	6.03 (CH)

[a] All resonances are singlets unless otherwise indicated. [b] Reference 3. [c] In CS_2. [d] In CD_3CN. [e] Reference 13. [f] In CCl_4.

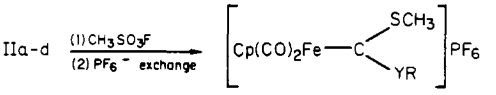
The thiocarbonyl complex $Cp(CO)_2Fe(CS)^+$ may be readily converted to thioester derivatives by reaction with alkoxides,[12,13] mercaptides, and selenides (eq 2). When this reaction is attempted with $PhTe^-$, much gas evolution results, and an unstable, intractable green tar is obtained. Nucleophilic attack by $PhTe^-$ appears to occur with CO ligand displacement to give the unstable green $Cp(CO)(CS)FeTePh$ and a very small amount of the desired thioester complex $Cp(CO)_2FeC(=S)TePh$ as suggested by IR spectra of the reaction solutions.



(2)

RY = CH_3O (IIa, 70%)[12]
= PhO (IIb)[13]
= PhS (IIc)
= PhSe (IId, 56%)

The thioester complexes IIa–d need not be isolated; IIb,c have been characterized only by their IR spectra. IR (IIb) (hexanes): 2042 (s), 1996 (s) cm^{-1}.[13] IR (IIc) (THF): 2028 (s), 1979 (s) cm^{-1}. Reaction of the crude thioester complexes with methyl fluorosulfonate followed by anion exchange affords cationic carbene complexes in reasonable yield (eq 3). Methyl



(3)

YR = OCH_3 (IIIa, 41%)
= OPh (IIIb, 43%)
= SPh (IIIc, 75%)
= SePh (IIId, 74%)

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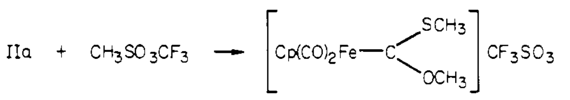
Table III. ^{13}C NMR Spectra of the New Complexes and Other Pertinent Carbene Complexes in Acetone-d_6 (singlets, ppm)

complex	C(carbene)	CO	C_5H_5	OCH_3	SCH_3	C_6H_5	other resonances
Ia[a]	303.1	209.5	88.6		29.6		
Ia[a,b]	304.3	210.1	89.2		30.3		
Ib[b]	304.2	210.5	89.4		30.3		
IIIb	301.1	209.0	89.4		22.5	159.7, 131.6, 129.6, 122.6	
IIIb[b]	301.2	208.9	89.4		23.0	159.6, 131.7, 129.7, 122.6	
IIIc	308.9	209.6	89.3		30.4	134.4, 133.0, 131.3	
IIIc[c]	309.4	209.7	89.6		31.3	135.3, 134.8, 133.6, 131.8	
IIId[c]	321.0	209.8	90.0		34.4	136.4, 134.9, 133.0, 132.1	
IV	297.9	210.0	89.2	71.8	21.5		
V		212.5	88.6		28.9		
VIIa		209.6	88.7		26.6	134.5, 131.5, 131.0, 129.5	
VIIb		210.2	87.9			131.4, 131.2, 130.6, 128.4	17.8 ($SeCH_3$)
VIIIa	294.7	209.8	89.7				48.2 (2 SCH_2)
VIIIb	283.7	210.9	89.4				39.6 (2 SCH_2), 19.1 (CH_2)
IX[d]	251.9	210.3	88.1	63.6			
Xa	251.8	210.3	88.2	63.8			
Xa[b]	251.9	210.2	88.1	63.9			
Xb	250.4	210.5	88.3	63.4			74.9 (OCH_2), 14.3 (CH_3)
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_2N}H]\}PF_6$[a]	200.0	212.2	87.6				46.4 (2 CH_2)
$\{Cp(CO)_2Fe[\overline{CNH(CH_2)_3N}H]\}PF_6$[a]	192.2	212.7	87.6				42.7 (2 CH_2), 20.1 (CH_2)

[a] Reference 3. [b] In CD_3CN. [c] In CD_3CN at 73 °C. [d] Reference 13.

triflate, $CH_3SO_3CF_3$, also alkylates the thioester complexes, but with IIb–d the carbene complexes obtained are difficult to purify as they do not crystallize readily. With IIa, however, the corresponding carbene complex is obtained in excellent yield by alkylation with $CH_3SO_3CF_3$ (eq 4). Entirely satisfactory elemental analyses could not be obtained for IIIc,d on independent samples even after several recrystallizations. However, their spectral data (Tables I–III), especially the characteristic carbene carbon resonance in the ^{13}C NMR spectra of IIIc,d, and their reactivity[14] clearly show their formulation as carbene complexes to be correct.



(4)

IV (92%)

Complex IIIc is quite stable toward air in the solid state. Complexes IIIb,d and especially IIIa and IV are less stable in this respect and are best stored at low temperatures (−20 °C). Samples of IIIa,b and IV stored in this manner, but handled periodically in air at room temperature, gradually develop small amounts of $CpFe(CO)_3^+$ as impurities. This may be due to a slight moisture sensitivity. Solutions of IIIa–d and IV, when not protected from the atmosphere, show little or no decomposition after storage for several days at −20 °C. Even at room temperature, decomposition of these solutions appears to be slow and is not noticeable for several hours.

In contrast to Ia,b and IIIb–d, the (methylthio)methoxycarbene complexes (IIIa and IV) display a marked thermal instability. When stored in air or under vacuum at room temperature, the yellow crystals of IIIa and IV become red-orange after approximately 12 h and eventually become deep red. At elevated temperatures (~100 °C), this conversion becomes very rapid and represents the formation of a sulfido-bridged binuclear complex (eq 5). The evolution of

$$\mathrm{IV} \xrightarrow[\text{(solid state)}]{\Delta} \underset{\mathrm{V}\ (61\%)}{\{[Cp(CO)_2Fe]_2SCH_3\}CF_3SO_3} + \underset{(12\%)}{\{CpFe(CO)_3\}CF_3SO_3} + CH_3SCH_3 + \ldots \quad (5)$$

CH_3SCH_3 is confirmed by its characteristic odor as well as by the mass spectrum and ^1H NMR spectrum of the volatile products from the reaction in eq 5, but the mechanism of this reaction is presently not understood as all of the side products have not been identified. In addition, IIIb shows no tendency to form V, even at higher temperatures (~150 °C). Refluxing IV in dried, degassed CH_3CN under an N_2 atmosphere for 10 h affords $Cp(CO)_2Fe(CH_3CN)^+$ (47%) and a large amount of unstable, unidentified decomposition product. The acetonitrile complex could result from the conversion of IV to $CpFe(CO)_3^+$ which is known to lose a CO ligand in refluxing acetonitrile.[15] The decomposition product appears to be the same as that observed when V is refluxed under the same conditions as for IV.

The production (eq 5) of V and $CpFe(CO)_3^+$ from IV would appear to be independent processes. The binuclear complex V may also be prepared by another route (eq 6). The iron

$$Cp(CO)_2FeSCH_3 + \{Cp(CO)_2Fe(acetone)\}CF_3SO_3 \rightarrow \underset{33\%}{\mathrm{V}} \quad (6)$$

sulfide complex is prepared from $Cp(CO)_2FeX$ (X = Cl, Br, I)[16] and CH_3S^-,[17] and $\{Cp(CO)_2Fe(acetone)\}X$ species may be obtained by oxidation of $[CpFe(CO)_2]_2$ with the appropriate silver(I) salt.[18] Complex V behaves very much like the ethyl derivative, $\{[Cp(CO)_2Fe]_2SCH_2CH_3\}^+$, which was prepared by a route analogous to that of eq 6.[19,20] Complex V shows three ν(CO) bands in its IR (CH_2Cl_2) spectrum (Table I); the two high-energy bands are sharp while the lower energy band is broad. This is due to rotational isomerism about the Fe–S bonds, as observed for $\{[Cp(CO)_2Fe]_2SCH_2CH_3\}^+$.[19] Three bands are observed, rather than the expected four, because the two asymmetric stretches are not resolved and give rise to one broad band.

The method outlined above (eq 2 and 3) for the preparation of carbene complexes from $Cp(CO)_2Fe(CS)^+$ cannot be extended to the $CpFe(CO)_3^+$ system. The alkoxycarbonyl

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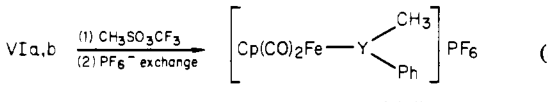
complex, $Cp(CO)_2FeC(=O)OCH_3$, is prepared by the reaction of $CpFe(CO)_3^+$ and CH_3O^- but decomposes to $[CpFe(CO)_2]_2$ fairly readily.[21] In addition, the reaction of $Cp(CO)_2FeC(=O)OCH_3$ with CH_3SO_3F or $CH_3SO_3CF_3$ affords $CpFe(CO)_3^+$ as the only isolable organometallic product by cleavage of the methoxy group. The reactions of $CpFe(CO)_3^+$ with PhS^- or $PhSe^-$ do not yield ester complexes but rather iron sulfide or selenide complexes by displacement of a CO ligand (eq 7). Complex VIa behaves as previously reported,[17]

$$CpFe(CO)_3^+ + PhY^- \rightarrow Cp(CO)_2FeYPh + CO(g) \qquad (7)$$

Y = S (VIa),
Se (VIb)

and VIb forms an unstable green oil with two ν(CO) absorptions in its IR (CH_2Cl_2) spectrum at 2025 (s) and 1979 (s) cm^{-1}. The crude products obtained by the reaction in eq 7 are reacted with $CH_3SO_3CF_3$ followed by anion exchange to give stable, crystalline iron thio- or selenoether complexes (eq 8). The spectroscopic data (Tables I–III) for VIIa are

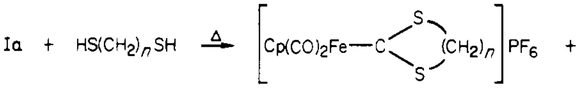


(8)

Y = S (VIIa, 24%)
= Se (VIIb, 34%)

nearly identical with those in a previous report.[18] The lower ν(CO) approximate force constant, k(CO),[22] for VIIb indicates that the $PhSeCH_3$ ligand has a lower π-acceptor/σ-donor ratio than the $PhSCH_3$ ligand.

Preparation of Carbene Complexes by "Heteroatom Metathesis". Complex Ia reacts with excess dithiol under reflux conditions by displacement of both CH_3S groups to give carbene complexes with cyclic dithiocarbene ligands (eq 9).



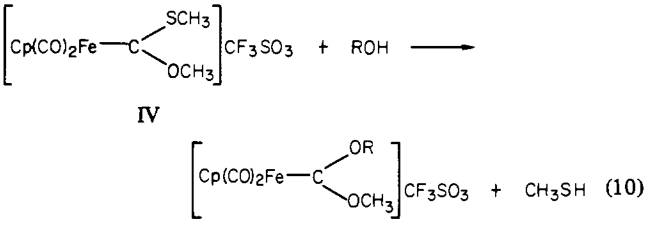
$n = 2$ (VIIIa, 78%)
= 3 (VIIIb, 60%)

$2CH_3SH$ (9)

Enough solvent, CH_2Cl_2 or acetone, is added to the systems so that reflux is maintained at 50–60 °C. Both reactions are complete within 3.5 h. The reaction of Ia and PhSH under similar conditions for 6 h produces a mixture of Ia, $Cp(CO)_2Fe[C(SCH_3)SPh]^+$, and $Cp(CO)_2Fe[C(SPh)_2]^+$. The mixture displays two ν(CO) bands in its IR (CH_2Cl_2) spectrum at 2058 (s) and 2020 (s) cm^{-1}. In the ^1H NMR (acetone-d_6) spectrum, the bis(phenylthio)carbene complex is the major component of the mixture with resonances at τ 2.29 (s, 2 C_6H_5) and 4.57 (s, C_5H_5). The carbene complexes VIIIa,b are yellow crystalline solids displaying the same stability and solubility characteristics as Ia.[3] The spectral properties of VIIIb are nearly identical with those reported for an impure sample of $\{Cp(CO)_2Fe[\overline{CS(CH_2)_3S}]\}BF_4$ prepared by α-hydride abstraction from $Cp(CO)_2Fe[\overline{C(H)S(CH_2)_3S}]$.[23]

The dioxo analogues of VIIIa,b could not be obtained. Refluxing Ia with ethylene glycol yields $CpFe(CO)_3^+$ as the only organometallic product, and no organometallic products could be separated from the excess diol after stirring Ia in 1,3-propanediol and a small amount of acetone for 19 h. Refluxing Ia in dried CH_3OH under an N_2 atmosphere for 2.5 h affords no dioxocarbene complexes but rather an 81% yield of $CpFe(CO)_3^+$. The dimethoxycarbene complex, $\{Cp(CO)_2Fe[C(OCH_3)_2]\}PF_6$ (IX),[13] also gives a high yield (88%) of $CpFe(CO)_3^+$ when refluxed with CH_3OH under similar conditions. Thus, dioxocarbene complexes may form when Ia is refluxed with CH_3OH or ethylene glycol, but they are not stable under these conditions and would decompose to $CpFe(CO)_3^+$.

The (methylthio)methoxycarbene complex, IV, reacts readily with methanol and ethanol by nucleophilic substitution of the CH_3S group (eq 10). This reaction is very similar to



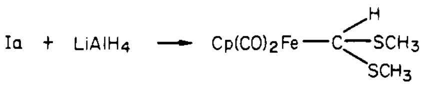
(10)

R = CH_3 (Xa, 89%)
= CH_2CH_3 (Xb, 57%)

that of IIIb with methanol in which both the CH_3S and the PhO groups are displaced to give IX in 44% yield.[13] Stirring IV in CH_3SH at room temperature under slight pressure in a sealed tube for 12 h produces approximately equal amounts of Ib and $CpFe(CO)_3^+$. Complex Ib results from displacement of the CH_3O group of IV, and $CpFe(CO)_3^+$ may result from thermal decomposition of IV.

The dioxocarbene complexes IX and Xa,b are fairly stable, pale yellow crystalline solids. All show a tendency to slowly decompose to $CpFe(CO)_3^+$ on prolonged exposure to the atmosphere at room temperature in solution or in the solid state. Entirely satisfactory elemental analyses for Xb could not be obtained, but its spectral properties (Tables I–III), especially the characteristic carbene resonance in its ^{13}C NMR spectrum, clearly show its formulation as a carbene complex to be correct.

Preparation of an Unstable Secondary Carbene Complex. Complex Ia reacts rapidly with $LiAlH_4$ in THF to produce cyclopentadienyldicarbonylbis(methylthio)methyliron (XI) in nearly quantitative yield (eq 11). Complex XI is a low

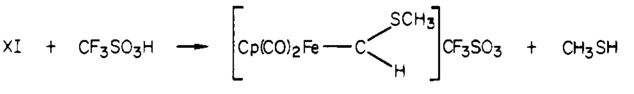


(11)

XI (91%)

melting, yellow, crystalline solid which is very stable in the solid state at low temperatures (−20 °C). Its properties are very similar to those of the related bis(organothio)methyliron complex $Cp(CO)_2Fe[\overline{C(H)S(CH_2)_3S}]$.[23]

The reaction of XI with strong acid, CF_3SO_3H, in Et_2O causes the immediate precipitation of a new secondary carbene complex (eq 12). This reaction has precedent in the related



XII

(12)

conversion of tris(organothio)methyliron complexes, $Cp(CO)_2Fe[C(SR)_3]$, to cationic dithiocarbene complexes by reaction with CF_3SO_3H.[23] The new secondary carbene complex, XII, has been characterized by its IR spectrum (Table I) only due to its low stability. Exposure of XII to moisture in the atmosphere, in solvents, or in the acid reagent employed causes the rapid formation of $CpFe(CO)_3^+$. This may proceed through a Fischer–Tropsch type intermediate, a secondary hydroxycarbene complex,[1] by nucleophilic attack of H_2O on

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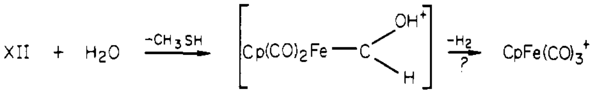
the carbene carbon followed by loss of CH_3SH and possibly H_2 (eq 13).



(13)

The IR spectrum of XII is consistent with its formulation as a secondary carbene complex. The replacement of one π-donating CH_3S group in Ib with a H atom would induce more M → C π back-bonding and raise the $\nu(CO)$ frequencies. Comparison of Ib and XII show this indeed to be the case with XII having a $k(CO)$ value which is 0.19 mdyn/Å larger than that of Ib. The IR spectrum of XII also compares favorably with its oxygen analogue, $\{Cp(CO)_2Fe[C(OCH_3)H]\}PF_6$ (XIII).[24] In going from a dithiocarbene complex (Ia,b, IIIc) to a dioxocarbene (IX, Xa) or a thiooxocarbene complex (IIIb), an increase in $\nu(CO)$ and $k(CO)$ is observed. In accordance with this trend, the $k(CO)$ value of XIII is 0.30 mdyn/Å higher than that of XII. Like complex XII, complex XIII is also moisture sensitive[24] but hydrolyzes much slower than does XII. This difference in rate of hydrolysis may be due to the relatively poor leaving-group characteristics of the alkoxy group in nucleophilic substitution reactions.[25]

Spectroscopic Analysis. The IR, ^1H NMR, and ^{13}C NMR spectra of the complexes prepared herein and those discussed below are presented in Tables I–III, respectively. All $\nu(CO)$ force constants, $k(CO)$, are calculated by the method of Cotton and Kraihanzel.[22]

Previous reports have shown that a linear correlation exists between $k(CO)$ and the ^{13}C NMR chemical shift of the CO ligands, $\delta(CO)$, for $Cp(CO)_2FeX$[26] and $Cp(CO)_2FeL^+$[27] derivatives; $\delta(CO)$ moves to lower field as M–CO π back-bonding increases.[4] No such correlation exists among the various $Cp(CO)_2Fe[carbene]^+$ complexes. As a group, however, these complexes come reasonably close to fitting the previously observed correlation,[26,27] but the CO ligands are all slightly (0.2–2.5 ppm) more shielded in the ^{13}C NMR spectra than would be predicted from their $k(CO)$ values. The correlation between $k(CO)$ and $\delta(CO)$ for $Cp(CO)_2FeX$ derivatives fails when $X = SiR_3$, GeR_3, or SnR_3, and this was accounted for by possible π bonding between Fe and the group 4 ligands.[26] The lack of correlation between $k(CO)$ and $\delta(CO)$ for the carbene complexes may also be a consequence of an Fe–C(carbene) π interaction. It is interesting to note that the diaminocarbene complexes, where Fe–C(carbene) π bonding should be at a minimum due to the strong nitrogen π-donor ability,[3,28–31] come the closest to fitting the previously observed correlation.[26,27]

The ^{13}C NMR chemical shift of the carbene carbon, δ(carbene), has been shown to be more sensitive to changes in the electronic environment than $\delta(CO)$[7] and may be a measure of the degree of π donation from the heteroatomic substituents to the carbene carbon. For complexes of the type $(CO)_5CrC(YR)R$,[1] a large upfield shift was noted in δ(carbene) on changing the YR group from an alkoxy to the better π-donating NR_2 group.[7] It was also found that δ(carbene) moves to higher field with increasing π-donor ability of the aryl carbene substituent for a series of $(CO)_5MC(p\text{-}C_6H_4X)OCH_3$ (M = Cr, W) complexes.[32] These trends seem logical considering that the low-field resonance of the carbene carbon is due, in part, to its presumed electron-deficient nature.[6,7,29] Thus, relieving this electron deficiency by π donation from the carbene substituents could cause an upfield shift in δ(carbene).

However, no correlation between $k(CO)$ and δ(carbene) exists for the $Cp(CO)_2Fe[carbene]^+$ complexes. In fact, the use of $k(CO)$ and δ(carbene) data by themselves leads to very different conclusions concerning the π-donation ability of the various heteroatomic carbene substituents. Thus, it appears that $k(CO)$ is the most reliable parameter of the bonding in these $Cp(CO)_2Fe[carbene]^+$ complexes.

The $k(CO)$ values for the iron carbene complexes are probably related to the π-acceptor/σ-donor ratio of the carbene ligand which is, in turn, inversely related to the π-donor ability of the carbene substituents. Therefore, higher $k(CO)$ values are indicative of a lower degree of carbene π stabilization by the heteroatomic substituents.

The $k(CO)$ values of IIIb–d indicate that Se is slightly better than S and both are better than O in π-donor ability, while the δ(carbene) values for these complexes and for $(CO)_5W\text{-}C(YCH_3)CH_3$ (Y = O, 332.9; Y = S, 332.5; Y = Se, 355.5 ppm)[8] suggest the opposite trend. Infrared data for complexes Ia,b, IX, Xa,b, and $\{Cp(CO)_2Fe[C(SCH_3)SCH_2CH_3]\}PF_6$ support the trend that S has a greater π-donation ability than O. The $k(CO)$ values for the dioxocarbene complexes are all higher than the corresponding dithiocarbene complexes while the thiooxocarbene complexes have intermediate $k(CO)$ values.

The ambient-temperature ^1H NMR spectra of IIIc,d show broad singlets for the Ph and Cp groups while IIIb shows a well-resolved multiplet for the Ph group and a sharp singlet for the Cp ligand. In addition, δ(carbene) cannot be observed for IIId and is quite broad for IIIc in the ambient-temperature ^{13}C NMR spectra while δ(carbene) for IIIb is sharp. The δ(carbene) resonances for IIIc,d become sharp singlets when the ^{13}C NMR spectra are obtained at elevated temperatures (73 °C). This behavior may be due to syn–anti isomerization by restricted rotation about the C(carbene)–YPh (Y = S, Se) bonds with coalescence occurring near the NMR probe temperature (~30 °C). The increased barrier for such a rotation in IIIc,d as compared to Ia (coalescence at −2.5 °C)[3] is likely due to the steric bulk of the Ph group and/or slightly better π donation from the PhY groups,[33] compared to the CH_3Y carbene substituents, as indicated by the $k(CO)$ values of Ia and IIIa–c. The fact that IIIb does not show this behavior at ambient temperatures may be a consequence of the weaker O → C(carbene) π donation. It should be noted that any barrier to rotation around the Fe–C(carbene) bond in these complexes should be lower, because of heteroatom π stabilization, than that reported for the methylidene analogues, $Cp(L)_2Fe{=}CH_2^+$.[34]

Comparison of the $k(CO)$ values for complexes VIIIa,b and their diamino analogues, $\{Cp(CO)_2Fe[\overline{CNH(CH_2)_nNH}]\}PF_6$ ($n = 2, 3$), indicate a significantly stronger π donation from nitrogen to the carbene carbon than from sulfur. For these complexes, $\delta(CO)$ and δ(carbene) follow the expected trends with $\delta(CO)$ shifted to lower and δ(carbene) to higher field for the diaminocarbene complexes.

There is also a difference in $k(CO)$ values between VIIIa and VIIIb which indicates a significantly poorer S → C-

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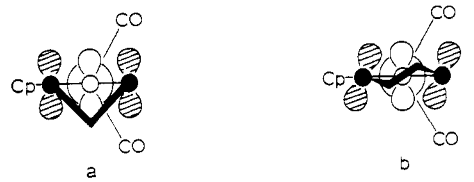

Figure 1. Newman-type projections down the Fe–C(carbene) bond axis for (a) $\mathrm{Cp(CO)_2Fe[\overline{CS(CH_2)_3S}]^+}$ and (b) $\mathrm{Cp(CO)_2Fe[\overline{CS(CH_2)_2S}]^+}$.

(carbene) π donation in the five-membered ring carbene ligand of VIIIa. The same trend is seen in the *k*(CO) values for the cyclic diaminocarbene complexes, although the difference between the five- and six-membered ring carbene ligands is smaller for these complexes.

Better π donation from the heteroatoms to the carbene carbon in the six-membered ring complexes may be rationalized by comparing ring conformations in the five- and six-membered ring carbene ligands (Figure 1). Models show that the ring strain introduced by the planarity of the carbene linkage (both heteroatoms and the carbene carbon are sp^2 hybridized) may be easily alleviated by the six-membered ring on the assumption of a half-chair conformation (Figure 1a). This leaves the filled p_z orbitals of the heteroatoms coplanar with the p_z of the carbene carbon allowing for good π overlap. In the five-membered ring, the strain may only be alleviated by a twisting of the ethylene linkage (Figure 1b). This would tend to force the filled p_z orbitals of the heteroatoms out of coplanarity with the p_z orbital of the carbene carbon and, thus, reduce the π overlap of these orbitals. Another, but related, explanation would suggest that the strain in the five-membered ring complex would cause rehybridization of the sulfur atoms from sp^2 toward sp^3 and thereby lower their π-donor ability. This explanation, referred to as the "hinge effect", accounts for several observations for cyclic and acyclic phosphates and phosphites.[35]

Conclusion

Infrared data indicate that the order of decreasing π donation to the carbene carbon by the heteroatoms in $\mathrm{Cp(CO)_2Fe[C(XR)YR]^+}$ carbene complexes is N ≫ Se ≥ S > O and that the differences between Se, S, and O are small. This compares well with previously reported trends.[3,25,28,36–38] The large range of δ(carbene) values (~130 ppm) and small range of δ(CO) values (~4 ppm) observed for these complexes further confirms the higher sensitivity of δ(carbene) to changes in the electronic environment.[7] The lack of correlation with *k*(CO) suggests that δ(carbene) resonances are best used at this time to confirm the presence of a carbene ligand and not for discussions of bonding. Exceptions to this may be when the π-donation differences are large such as N vs. Se, S, or O or when the atoms directly bound to the carbene carbon are not changed such as in the series of complexes $\mathrm{(CO)_5MC(\textit{p}\text{-}C_6H_4X)OCH_3}$ (M = Cr, W).[32] Some definite trends in δ(carbene) are observed as the heteroatoms are changed for the $\mathrm{Cp(CO)_2Fe[C(XR)YR]^+}$ carbene complexes: the selenothiocarbene derivative resonates at approximately 320 ppm, dithio- and thiooxocarbene complexes between 280 and 310 ppm, dioxocarbene complexes at approximately 250 ppm, and diaminocarbene derivatives between 190 and 200 ppm. It is also apparent that ring strain and conformation play an important role in π stabilization of cyclic carbene ligands.

Experimental Section

General Information. Reagent grade chemicals were used without further purification; $\mathrm{Cp(CO)_2FeC({=}S)SCH_3}$,[9] $\mathrm{Cp(CO)_2FeC({=}S)OCH_3}$,[12] $\mathrm{\{Cp(CO)_2Fe(CS)\}CF_3SO_3}$,[13] $\mathrm{\{CpFe(CO)_3\}CF_3SO_3}$,[13] $\mathrm{\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6}$ (Ia),[3] and $\mathrm{\{Cp(CO)_2Fe[C(OCH_3)_2]\}PF_6}$ (IX)[13] were prepared as reported previously. Tetrahedrofuran (THF) was distilled from sodium benzophenone ketyl under N_2 immediately prior to use. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer. Routine ^1H NMR spectra were recorded on a Perkin-Elmer Hitachi R-20B spectrometer, and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer; $\mathrm{Cr(acac)_3}$ (~0.1 M) was added to the ^{13}C samples to reduce data collection time.[39] Tetramethylsilane ($\mathrm{Me_4Si}$) was employed as the internal standard for all NMR spectra.

Preparation of the Complexes. $\mathrm{\{Cp(CO)_2Fe[C(SCH_3)_2]\}CF_3SO_3}$ (Ib). A 50-mL solution of $\mathrm{CH_2Cl_2}$ containing $\mathrm{Cp(CO)_2FeC({=}S)SCH_3}$ (2.50 g, 9.32 mmol) and $\mathrm{CH_3SO_3CF_3}$ (1.05 mL, 9.32 mmol) was allowed to stir for 1 h. The brownish solution was then evaporated to dryness, and the resulting residue was washed with $\mathrm{Et_2O}$. Crystallization of this residue from $\mathrm{CH_2Cl_2}$ with $\mathrm{Et_2O}$ at -20 °C afforded 3.5 g (87%) of Ib as large, dark yellow crystals, mp 76–78 °C. Anal. Calcd for $\mathrm{C_{11}H_{11}F_3FeO_5S_3}$: C, 30.57; H, 2.57. Found: C, 30.80; H, 2.61.

$\mathrm{Cp(CO)_2FeC({=}S)SePh}$ (IId). An N_2 atmosphere was required for this preparation. A solution of 25 mL of THF containing PhSeSePh (0.16 g, 0.51 mmol) was stirred with 5 mL of Na/Hg (0.050 g of Na, 2.2 mmol) until the yellow color of the PhSeSePh disappeared (~15 min). The amalgam was removed, and $\mathrm{\{Cp(CO)_2Fe(CS)\}CF_3SO_3}$ (0.37 g, 1.0 mmol) was added to the cloudy $\mathrm{PhSe^-}$/THF solution. A deep red-brown color developed rapidly. This solution was stirred for 10 min and was then evaporated to a red-brown oil. The N_2 atmosphere was not necessary beyond this point. The oil was extracted with $\mathrm{CS_2}$ until the extracts were colorless (~30 mL). These extracts were filtered and evaporated to give a red-orange solid which was crystallized from a minimum amount of hexanes by cooling the sample to -20 °C. Large red crystals of IId (0.21 g, 56%) were obtained; mp 76–79 °C. Anal. Calcd for $\mathrm{C_{14}H_{10}FeO_2SSe}$: C, 44.59; H, 2.67. Found: C, 44.68; H, 2.77.

$\mathrm{\{Cp(CO)_2Fe[C(SCH_3)OCH_3]\}PF_6}$ (IIIa). A sample of $\mathrm{Cp(CO)_2FeC({=}S)OCH_3}$ (0.300 g, 1.19 mmol) was stirred with $\mathrm{CH_3SO_3F}$ (120 μL, 1.48 mmol) in 15 mL of $\mathrm{CH_2Cl_2}$ for 30 min. The yellow-brown solution was then evaporated to a yellowish oil which was washed with $\mathrm{Et_2O}$. This oil was dissolved in a minimum amount of acetone, placed on an anion-exchange column (Amberlite IRA-400, 35 × 1 cm) in the $\mathrm{PF_6^-}$ form, and eluted slowly with acetone. The yellow acetone fraction was collected and evaporated to dryness. The resulting yellow residue was crystallized from $\mathrm{CH_2Cl_2}$ with $\mathrm{Et_2O}$ at -20 °C to give 0.20 g (41%) of IIIa as golden yellow crystals, mp 105 °C (conversion to $\mathrm{PF_6^-}$ salt of V). Anal. Calcd for $\mathrm{C_{10}H_{11}F_6FeO_3PS}$: C, 29.15; H, 2.69. Found: C, 29.21; H, 2.72.

$\mathrm{\{Cp(CO)_2Fe[C(SCH_3)OPh]\}PF_6}$ (IIIb). An N_2 atmosphere was required in this preparation. Phenol (0.060 g, 0.64 mmol) and NaH (50% mineral oil dispersion, 0.026 g, 0.54 mmol) were reacted in 40 mL of THF for 12 h. To this solution was added $\mathrm{\{Cp(CO)_2Fe(CS)\}CF_3SO_3}$ (0.20 g, 0.54 mmol), and the mixture was stirred for 1 h. The solution was then evaporated to a dark oil. The N_2 atmosphere was no longer required, and the oil was extracted with $\mathrm{CS_2}$ until the extracts were colorless (~30 mL). After filtration, these extracts were evaporated to a dark oil. The oil was dissolved in 20 mL of $\mathrm{CH_2Cl_2}$ and was stirred with $\mathrm{CH_3SO_3F}$ (50 μL, 0.62 mmol) for 1.5 h. The resulting dark solution was evaporated to an oil which was washed with $\mathrm{Et_2O}$. This crude $\mathrm{SO_3F^-}$ salt was converted to its $\mathrm{PF_6^-}$ salt and crystallized by the method used for IIIa. The yield of IIIb, as clear yellow needles, was 0.11 g (43%); mp 153–154 °C. Anal. Calcd for $\mathrm{C_{15}H_{13}F_6FeO_3PS}$: C, 38.00; H, 2.76. Found: C, 37.64; H, 2.75.

$\mathrm{\{Cp(CO)_2Fe[C(SCH_3)SPh]\}PF_6}$ (IIIc). This complex was prepared in the same manner as IIIb. Thus, PhSH (60 μL, 0.58 mmol) and $\mathrm{\{Cp(CO)_2Fe(CS)\}CF_3SO_3}$ (0.20 g, 0.54 mmol) yielded 0.20 g (75%) of IIIc as bright yellow crystals, mp 155–157 °C. Anal. Calcd for $\mathrm{C_{15}H_{13}F_6FeO_2PS_2}$: C, 36.75; H, 2.67. Found: C, 34.75; H, 2.68.

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$\{Cp(CO)_2Fe[C(SCH_3)SePh]\}PF_6$ (IIId). A solution of 10 mL of CH_2Cl_2 containing IId (0.095 g, 0.25 mmol) and CH_3SO_3F (25 μL, 0.31 mmol) was stirred for 1.5 h. The resulting orange solution was then evaporated to dryness, and the residue was converted to the PF_6^- salt by the method used for IIIa. Small yellow crystals of IIId (0.10 g, 74%) were obtained; mp 142–145 °C. Anal. Calcd for $C_{15}H_{13}F_6FeO_2PSSe$: C, 33.54; H, 2.44. Found: C, 31.23; H, 2.42.

$\{Cp(CO)_2Fe[C(SCH_3)OCH_3]\}CF_3SO_3$ (IV). This complex was prepared by the method used for Ib. Starting with 0.271 g (1.08 mmol) of $Cp(CO)_2FeC({=}S)OCH_3$ and 125 μL (1.10 mmol) of $CH_3SO_3CF_3$ in 20 mL of CH_2Cl_2, 0.41 g (92%) of IV was isolated as yellow crystals, mp 92–95 °C (conversion to V). Anal. Calcd for $C_{11}H_{11}F_3FeO_6S_2$: C, 31.75; H, 2.66. Found: C, 31.55; H, 2.61.

$\{[Cp(CO)_2Fe]_2SCH_3\}CF_3SO_3$ (V). From $Cp(CO)_2FeSCH_3$ and $\{Cp(CO)_2Fe(acetone)\}CF_3SO_3$. This preparation required an N_2 atmosphere. A 40-mL solution of acetone (dried over $CaSO_4$ and N_2 saturated) containing $[CpFe(CO)_2]_2$ (0.416 g, 1.18 mmol) and $AgSO_3CF_3$ (0.604 g, 2.35 mmol) was stirred for 1 h. The maroon color of $[CpFe(CO)_2]_2$ was replaced by a red-orange color, and metallic silver was deposited as a silver mirror. This solution was then filtered through Celite to give a clear red solution. To this stirred solution was added 20 mL of acetone (dried over $CaSO_4$ and N_2 saturated) containing crude $Cp(CO)_2FeSCH_3$ (generated from $Cp(CO)_2FeCl$ (0.500 g, 2.35 mmol) and a slight excess of CH_3S^-[17]) dropwise over a 15-min period. The reaction was allowed to stir for an additional 30 min and was then evaporated to a red oil. The oil was washed with Et_2O and was crystallized from CH_2Cl_2 with Et_2O at -20 °C to give 0.43 g (33%) of V as dark red needles, mp 110–112 °C. Anal. Calcd for $C_{16}H_{13}F_3Fe_2O_7S_2$: C, 34.94; H, 2.38. Found: C, 34.58; H, 2.37.

From IV. A sample of IV (0.050 g, 0.12 mmol) was placed in a sealed, evacuated tube, and the tube was placed in an oil bath at 115 °C for 5 min. The yellow crystals rapidly changed to a red oil. After cooling of the red oil to room temperature, it was fractionally crystallized from CH_2Cl_2 with Et_2O at -20 °C to afford 5.0 mg (12%) of $\{CpFe(CO)_3\}CF_3SO_3$ as yellow crystals and 0.020 g (61%) of V as red needles. Anal. Calcd for $C_{16}H_{13}F_3Fe_2O_7S_2$: C, 34.94; H, 2.38. Found: C, 34.80; H, 2.37.

$\{Cp(CO)_2Fe[S(CH_3)Ph]\}PF_6$ (VIIa). An N_2 atmosphere was required for this synthesis. Diphenyl disulfide (0.031 g, 0.14 mmol) and $LiAlH_4$ (0.012 g, 0.32 mmol) were stirred together in 30 mL of THF until gas evolution ceased (~5 h). To this PhS^-/THF solution was added $\{CpFe(CO)_3\}CF_3SO_3$ (0.10 g, 0.28 mmol), and the mixture was stirred for an additional 1.5 h. Vigorous gas evolution was noted during this time. The reaction mixture was then filtered and evaporated to a red-brown oil. The use of the N_2 atmosphere was discontinued, and the oil was extracted with Et_2O until the extracts were colorless (~40 mL). These extracts were then filtered and evaporated to an oil which was dissolved in 10 mL of CH_2Cl_2. This CH_2Cl_2 solution was stirred with $CH_3SO_3CF_3$ (35 μL, 0.31 mmol) for 2 h. The resulting dark yellow solution was then evaporated to a yellow-brown oil which could not be made to crystallize. The oil was then dissolved in 15 mL of warm H_2O, and 15 mL of a saturated NH_4PF_6(aq) solution was added. A yellow powder precipitated immediately and was crystallized from CH_2Cl_2 with Et_2O at -20 °C to give VIIa (0.030 g, 24%) as bright yellow flakes, mp 145–148 °C. Anal. Calcd for $C_{14}H_{13}F_6FeO_2PS$: C, 37.69; H, 2.94. Found: C, 38.01; H, 2.98.

$\{Cp(CO)_2Fe[Se(CH_3)Ph]\}PF_6$ (VIIb). This complex was prepared by the method used for VIIa. Thus, PhSeSePh (0.045 g, 0.14 mmol) and the same quantities of other reagents as used for VIIa produced 0.047 g (34%) of VIIb as small yellow crystals, mp 141–143 °C. Anal. Calcd for $C_{14}H_{13}F_6FeO_2PSe$: C, 34.11; H, 2.66. Found: C, 34.11; H, 2.64.

$\{Cp(CO)_2Fe[\overline{CS(CH_2)_2S}]\}PF_6$ (VIIIa). A solution consisting of 5 mL of acetone (dried over $CaSO_4$), 1,2-ethanedithiol (3.00 mL, 35.8 mmol), and Ia (1.00 g, 2.34 mmol) was refluxed under an N_2 atmosphere for 3 h. The resulting orange solution was evaporated to an oil (~3 mL). The addition of 40 mL of Et_2O to this oil followed by cooling of the solution to -20 °C caused the formation of a yellow precipitate. This precipitate was crystallized from CH_2Cl_2 with Et_2O at -20 °C to afford 0.78 g (78%) of VIIIa as dark yellow crystals, mp 109–110 °C. Anal. Calcd for $C_{10}H_9F_6FeO_2PS_2$: C, 28.19; H, 2.13. Found: C, 28.48; H, 2.21.

$\{Cp(CO)_2Fe[\overline{CS(CH_2)_3S}]\}PF_6$ (VIIIb). A 10-mL solution of CH_2Cl_2 (dried over $CaSO_4$) containing Ia (1.00 g, 2.34 mmol) and 1,3-propanedithiol (3.00 mL, 29.9 mmol) was refluxed under an N_2 atmosphere for 3.5 h. The resulting black solution was evaporated to a yellow-green oil (~3 mL). Diethyl ether (40 mL) was added to the oil, and a greenish yellow precipitate formed when the solution was cooled to -20 °C. Crystallization of this precipitate from CH_2Cl_2, after treatment with decolorizing carbon, with Et_2O at -20 °C yielded 0.62 g (60%) of VIIIb as yellow needles, mp 166–168 °C. Anal. Calcd for $C_{11}H_{11}F_6FeO_2PS_2$: C, 30.02; H, 2.52. Found: C, 30.34; H, 2.65.

$\{Cp(CO)_2Fe[C(OCH_3)_2]\}CF_3SO_3$ (Xa). A sample of IV (0.102 g, 0.245 mmol) was dissolved in 10 mL of CH_3OH (dried over $CaSO_4$), and the solution was stirred for 30 min. The residue obtained after evaporation of this solution was crystallized from CH_2Cl_2 with Et_2O at -20 °C, and 0.087 g (89%) of Xa was obtained as small, pale yellow crystals, mp 128–131 °C. Anal. Calcd for $C_{11}H_{11}F_3FeO_7S$: C, 33.02; H, 2.77. Found: C, 33.07; H, 2.77.

$\{Cp(CO)_2Fe[C(OCH_3)OCH_2CH_3]\}CF_3SO_3$ (Xb). A 0.094-g (0.23 mmol) sample of IV was dissolved in 10 mL of CH_3CH_2OH (dried over $CaSO_4$), and the solution was stirred for 1 h. The yellow oil obtained on evaporation of this solution was crystallized from CH_2Cl_2 with Et_2O at -20 °C to give 0.053 g (57%) of Xb as yellow needles, mp 66–68 °C. Anal. Calcd for $C_{12}H_{13}F_3FeO_7S$: C, 34.80; H, 3.16. Found: C, 33.89; H, 3.04.

$Cp(CO)_2Fe[C(SCH_3)_2H]$ (XI). This procedure required an N_2 atmosphere. A solution of 100 mL of THF containing Ia (0.10 g, 0.23 mmol) and $LiAlH_4$ (0.018 g, 0.47 mmol) was stirred for 20 min. This solution was then evaporated to a yellow oil which was extracted with hexanes until the extracts were colorless (~20 mL). These extracts were filtered and reduced in volume to 2 mL by evaporation under an N_2 stream. Cooling this hexanes solution to -20 °C afforded 0.053 g (91%) of XI as small, bright yellow crystals, mp 36–38 °C. Anal. Calcd for $C_{10}H_{12}FeO_2S_2$: C, 42.27; H, 4.26. Found: C, 42.29; H, 4.28.

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